Lens Engineering Development Department
Production Technology Headquarters
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OP-05

Oxidation durability of the Mo/Si multilayer with an oxide capping layer

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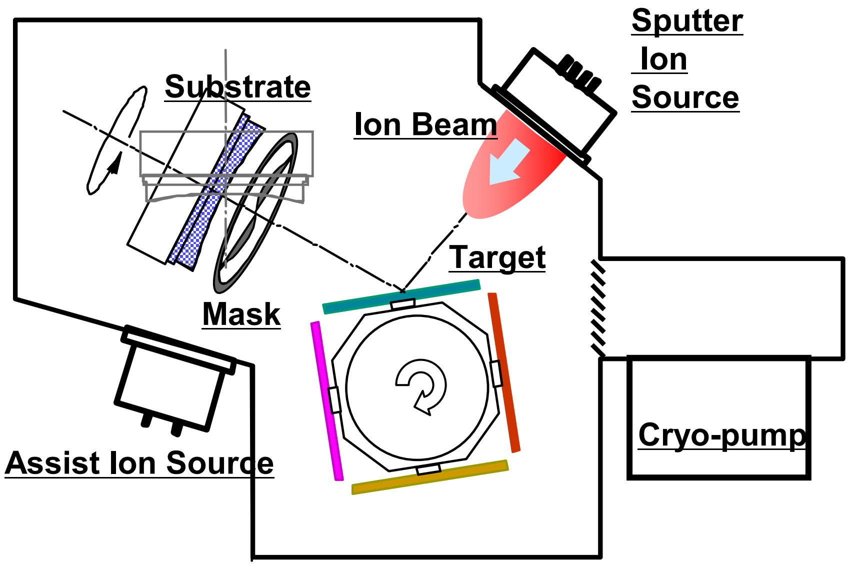
Introduction

Multilayer mirrors which have stable reflectance against high-power EUV radiation are required for HVM EUV exposure tools. It is known that degradation of the reflectance is caused by carbon deposition or oxidation due to the residual gas in the vacuum chamber. Carbon deposition can be cleaned by some methods, but oxidation is irreversible. In that sense oxidation is a serious problem to be solved by the different way from carbon deposition. To accomplish this, several kinds of capping layer which protect multilayer mirrors against oxidation have been developed. In this study, we investigated the durability of Mo/Si multilayers with several kinds of oxide capping layer prepared with ion-beam sputtering.

Preparation of multilayer mirror samples

Ion-beam sputtering apparatus



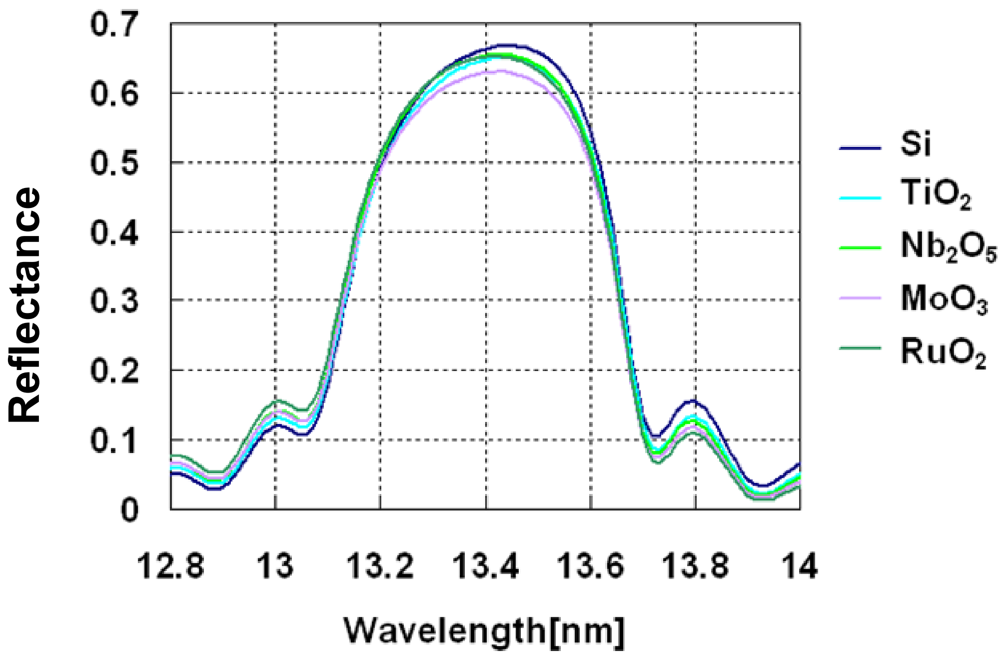
- Two ion sources (Sputter & Assist)
- Four targets
- Substrate size: max 400mm dia.
- Reactive sputtering for oxide materials

Multilayer mirror samples with several kinds of oxide capping layer were deposited on Si wafers using an ion-beam sputtering apparatus.

Multilayer mirror samples

Capping layer: TiO_2, Nb_2O_5, MoO_3, RuO_2
Thickness: ≈1.5nm
Reflective layers: Mo≈2.5nm, Si≈4.5nm, 50 pairs

Initial reflectance of multilayer mirrors



Capping layer	Peak reflectance
Si	66.7%
TiO_2	65.0%
Nb_2O_5	65.5%
MoO_3	63.0%
RuO_2	65.8%

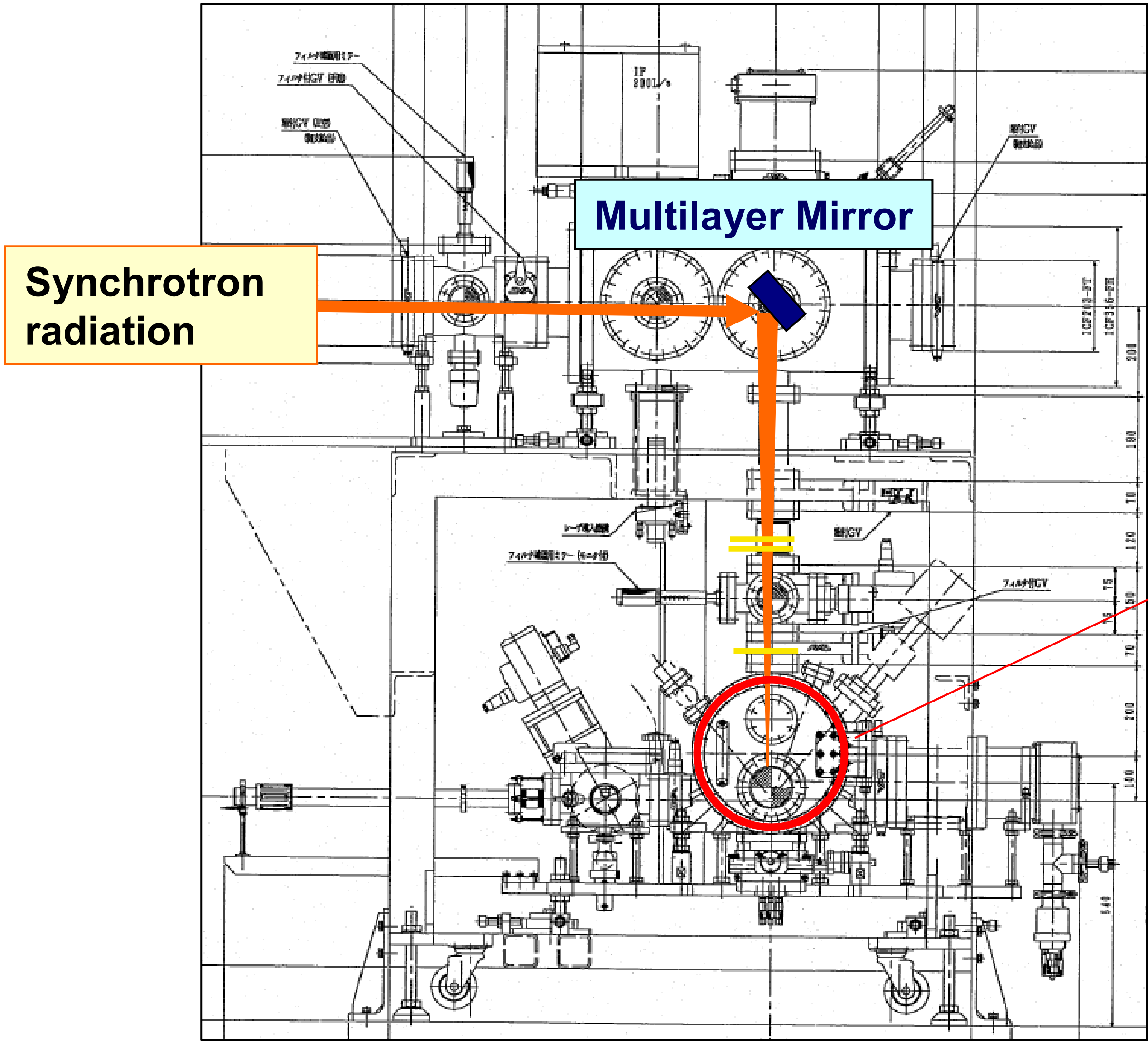
Reflectance was measured at the wavelength of 13.0nm using our in-house reflectometer* and measured data was converted to the normal-incidence reflectance at the wavelength of 13.5nm as shown in the above graph.

Initial reflectance of multilayer mirrors with oxide capping layer is lower than that with Si capping layer. It is considered to be due to the oxidation of Si layer under the capping layer during deposition.

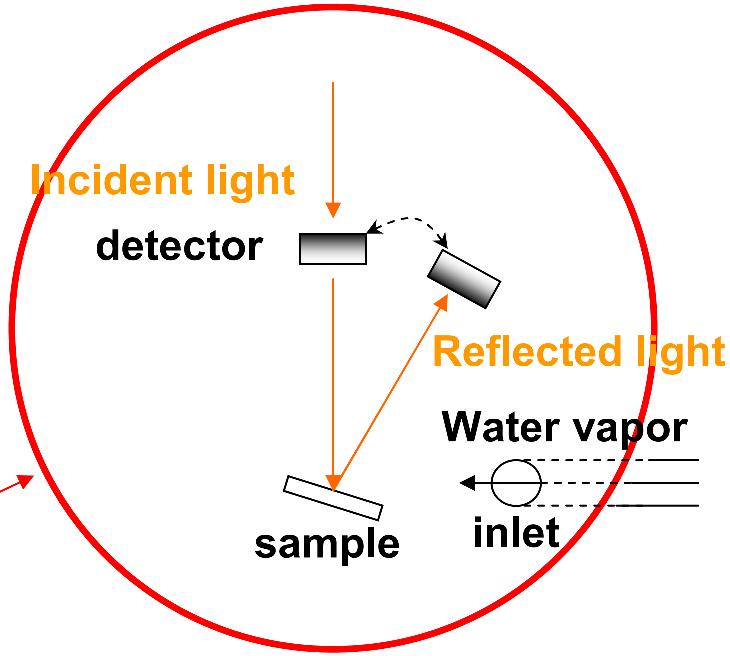
* N. Kandaka at. Al., "Development of an EUV reflectometer using a single line emission from a laser-plasma x-ray source", Proc. SPIE, 4343, 599, 2001.

EUV irradiation apparatus

Irradiation apparatus in *“SAGA Light Source”*



Irradiation chamber



Incidence angle to the sample : 10deg.

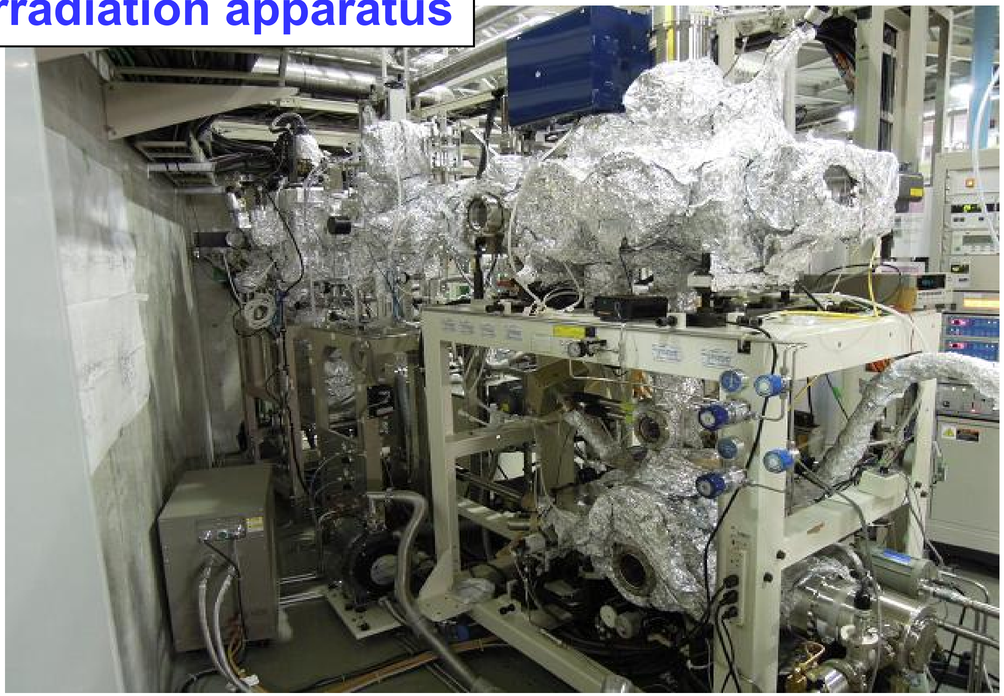
Change of reflectance is directly observed during irradiation.

EUV irradiation apparatus

Synchrotron radiation source (SAGA-LS)

Energy: 1.4GeV, Beam current: 100~300mA, Circumference: 75.6m

Irradiation apparatus



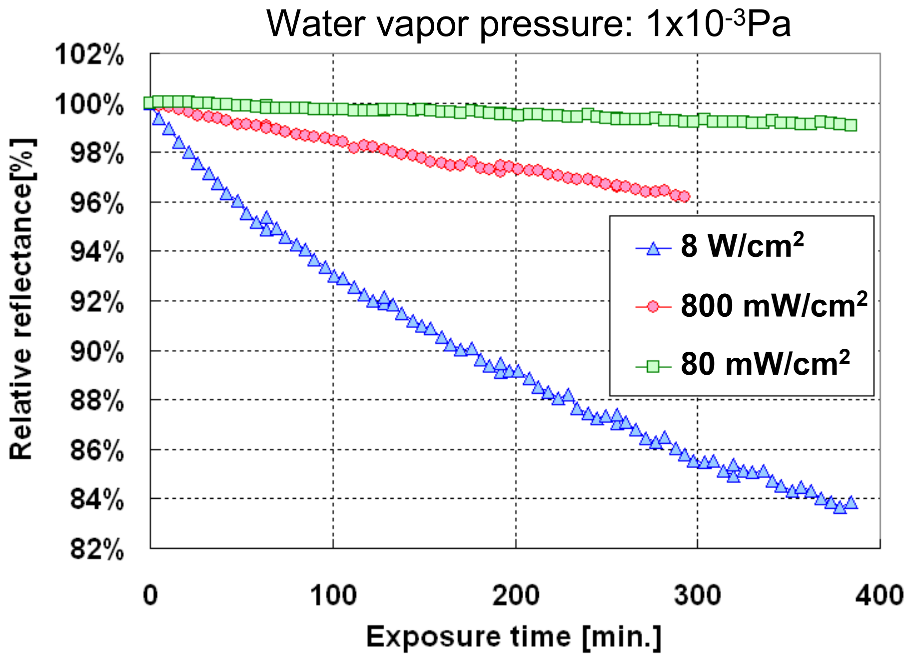
Irradiation condition

- Back pressure <3×10^{-7}Pa
- Water vapor pressure 1×10^{-3}Pa
- EUV intensity 8W/cm^2
- Exposure area ≈0.3mm^2

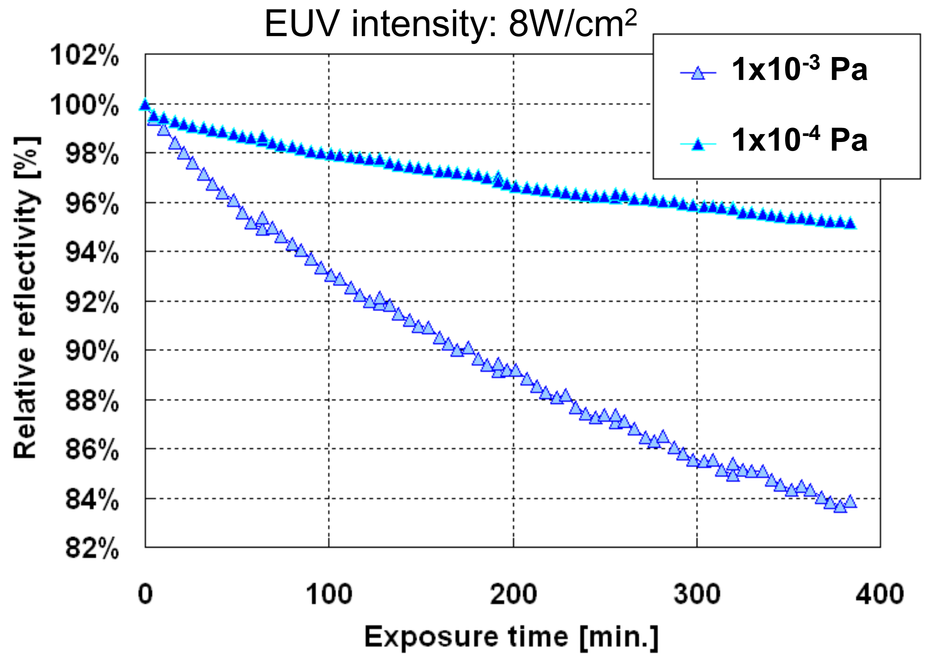
Sample holder

Reflectance change of Si-capped multilayer

EUV intensity dependence



Water pressure dependence



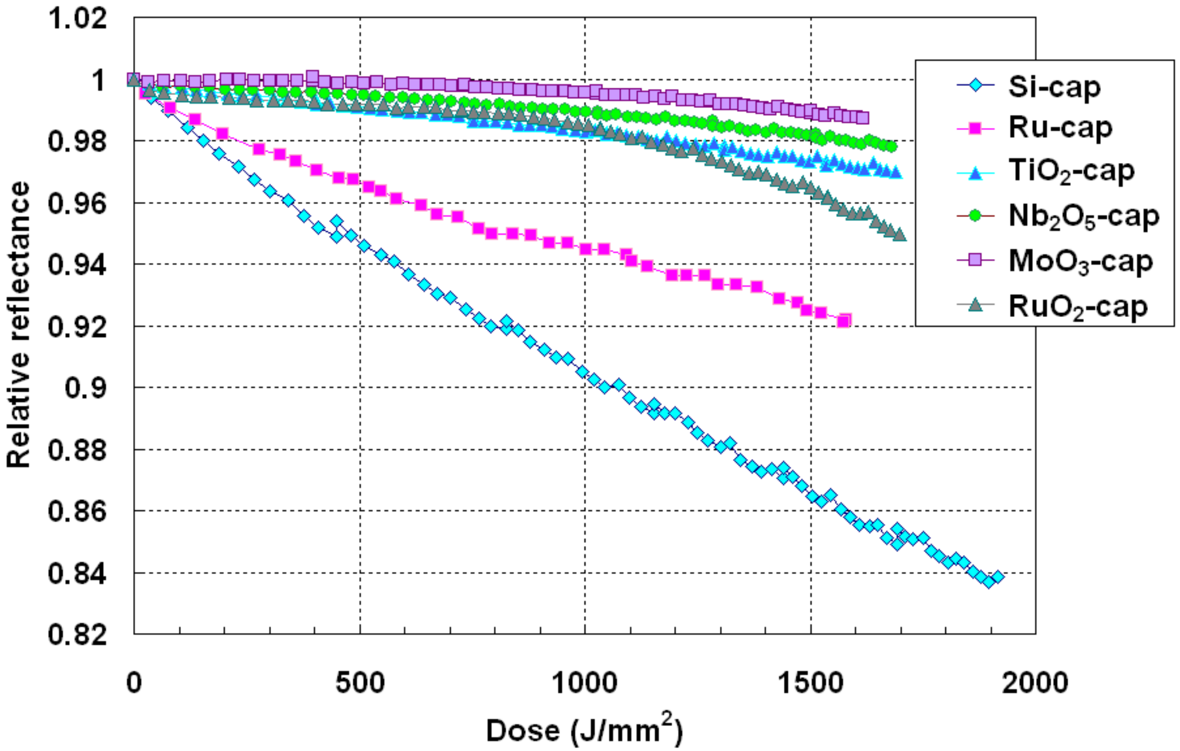
Degradation rate depends on EUV intensity and water pressure.
We adopted EUV intensity of $8W/cm^2$ and water vapor pressure of $1x10^{-3}Pa$ as a standard irradiation condition for accelerated test.
Oxidation model calculation was performed using these data.

See poster OP-02 “EUVL multilayer mirror oxidation modeling” by T. Hagiwara.

Reflectance change of oxide-capped multilayers

Irradiation condition

EUV intensity: 8W/cm^2, Water pressure: 1x10^{-3}Pa

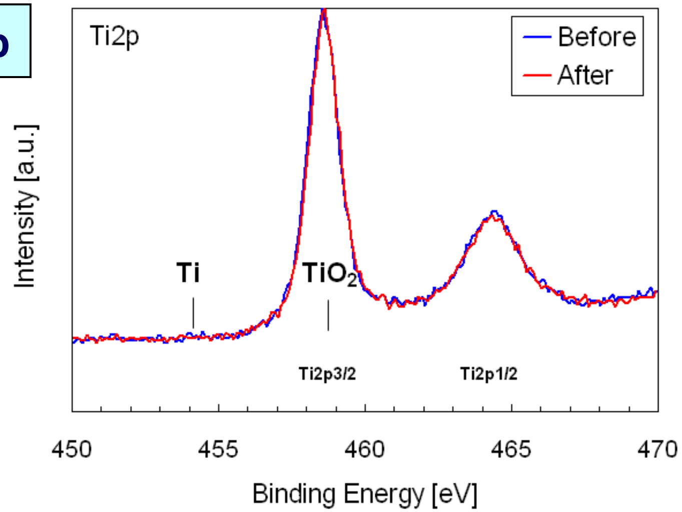


Cap	R_0	$\Delta R/R_0$ at 1.6kJ/mm^2
Si	66.7%	-14.5%
Ru	66.0%	-8.0%
TiO_2	65.0%	-1.9%
Nb_2O_5	65.5%	-1.0%
MoO_3	63.0%	-0.5%
RuO_2	65.8%	-4.6%

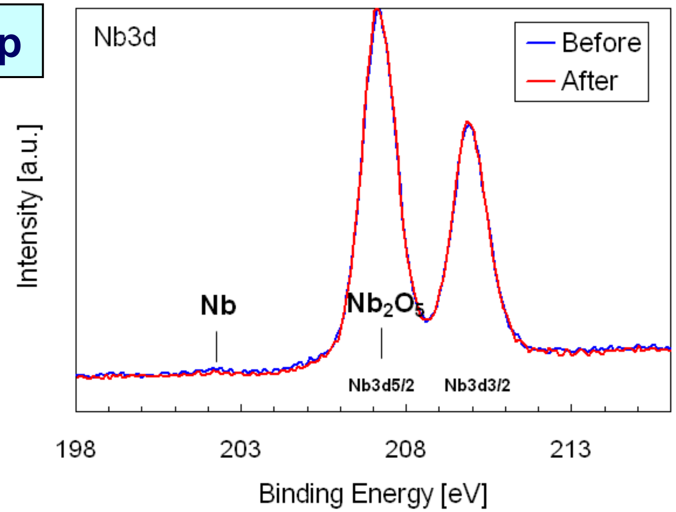
TiO_2, Nb_2O_5, MoO_3 and RuO_2 capped multilayers showed higher oxidation durability than Ru-capped multilayers. Especially, Nb_2O_5 and MoO_3 have good performance. Considering initial reflectance, Nb_2O_5 is more preferable material as capping layer than MoO_3.

XPS analysis of oxide capping layers

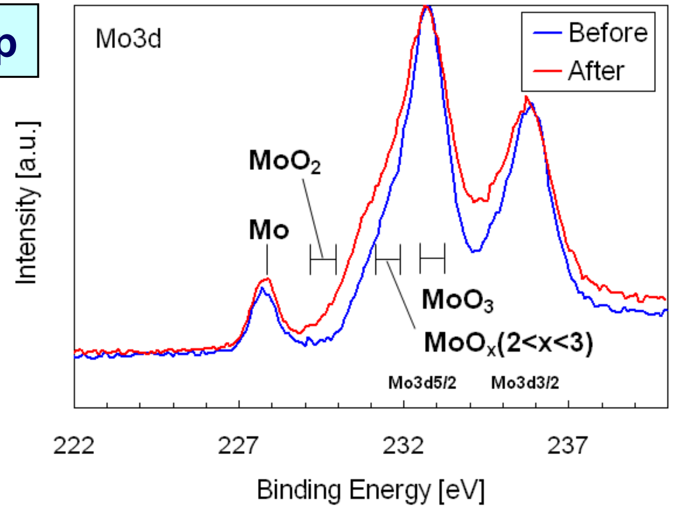
TiO_2-cap



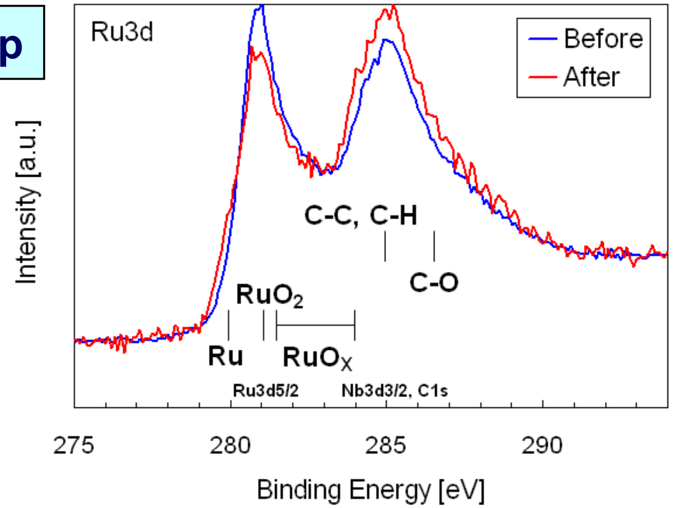
Nb_2O_5-cap



MoO_3-cap



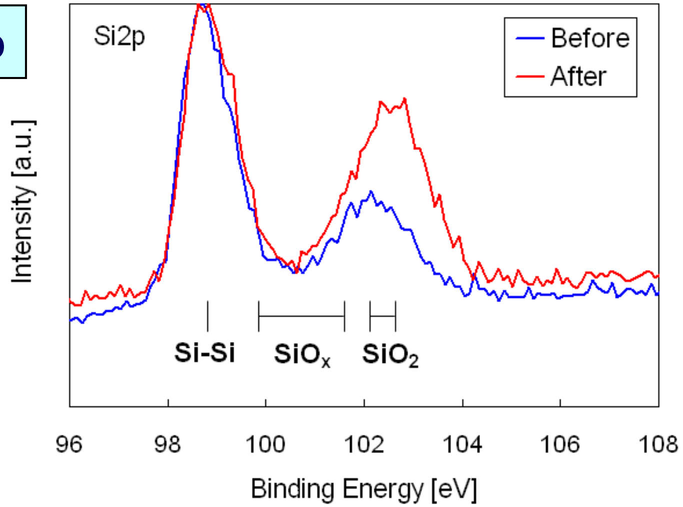
RuO_2-cap



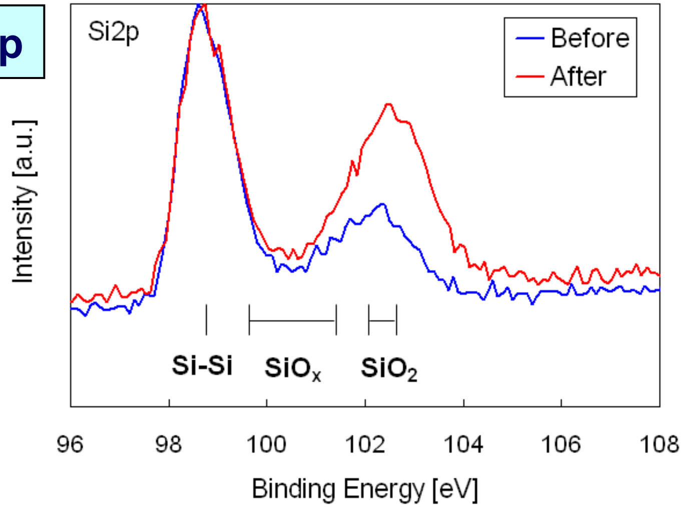
TiO_2 and Nb_2O_5 are very stable against EUV irradiation.
In contrast, reduction was observed in MoO_3 and RuO_2.

XPS analysis of Si layers under capping layers

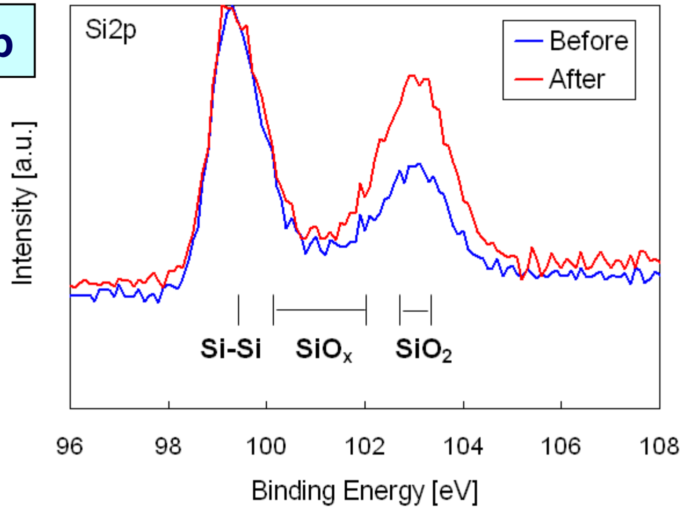
TiO_2-cap



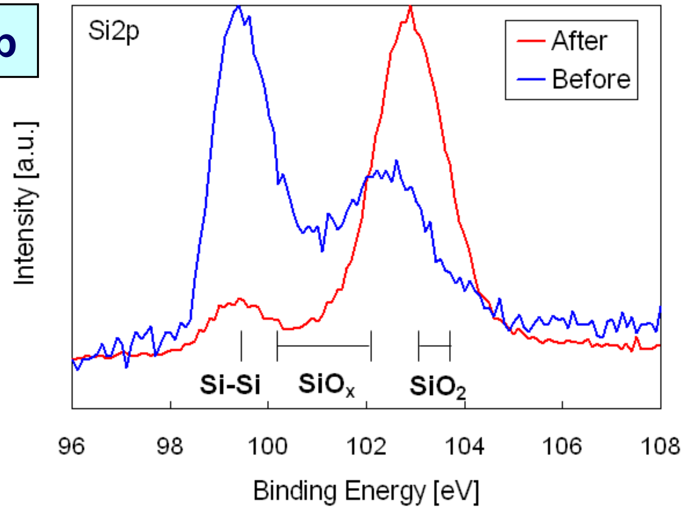
Nb_2O_5-cap



MoO_3-cap



RuO_2-cap

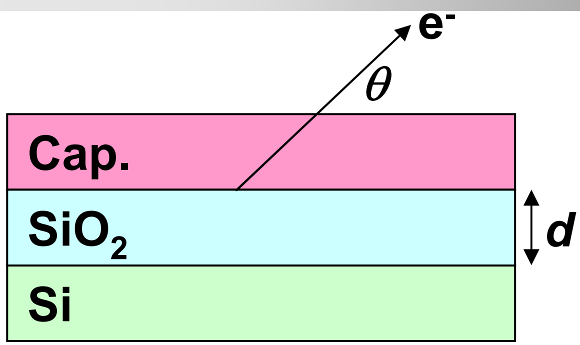


Peak of SiO_2 was observed in every samples even before EUV irradiation.
The peak intensity of SiO_2 was increased after EUV irradiation in every samples.

Oxidation of Si layer under capping layer

Calculation of SiO_2 thickness from XPS

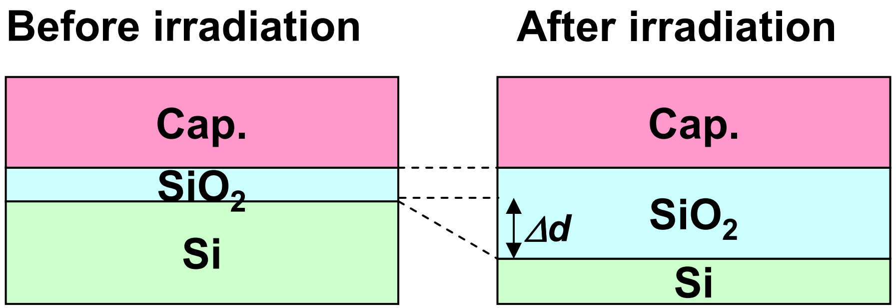
$$d = \lambda \sin\theta \cdot \ln\left(\frac{I_{SiO_2}}{I_{Si}} \cdot \frac{n_{Si}}{n_{SiO_2}} + 1 \right)$$

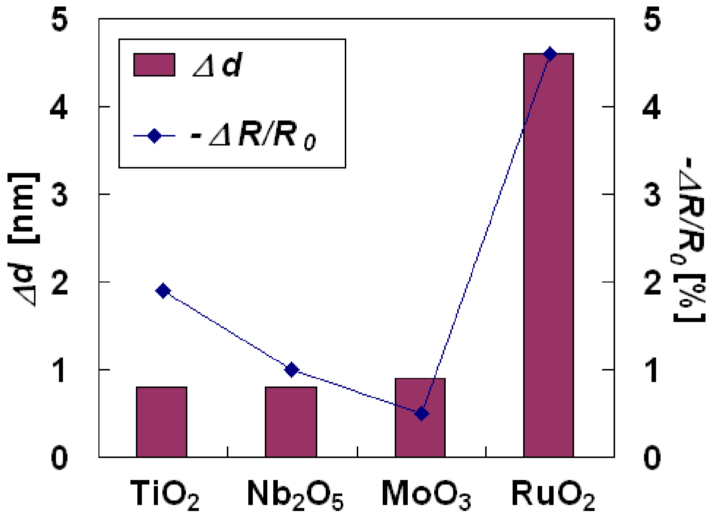


λ : wavelength (0.834nm), θ : escape angle of electron (45deg.)

I : intensity of photo-electron signal, n : density (Si:2.33g/cm^3, SiO_2:1.24g/cm^3)

Schematic view of oxidation





Oxidation of Si layer under capping layer can be roughly estimated from XPS data. In the case of RuO_2 capping layer, oxidation of Si layer after EUV irradiation degrades reflectance.

Summary of the experimental results

Capping layer	Initial reflectance R_0	Change of reflectance* $\varDelta R/R_0$	Stability (Reduction)	SiO_2 growth under capping layer
Nb_2O_5	65.5% ☺	-1.0% ☺	○ ☺	+0.8nm ☺
TiO_2	65.0% ☺	-1.9% ☹	○ ☺	+0.8nm ☺
RuO_2	65.8% ☺	-4.6% ☹	× ☹	+4.6nm ☹
MoO_3	63.0% ☹	-0.5% ☺	× ☹	+0.9nm ☺

* water pressure $1\text{x}10^{-3}$Pa, dose 1.6kJ/mm^2

MoO_3 capped multilayers showed high oxidation durability but their initial reflectance is relatively low.
RuO_2 capped multilayers showed large degradation of reflectivity.
Reduction was observed for RuO_2 and MoO_3 after EUV irradiation.
Nb_2O_5 capped multilayers showed better oxidation durability than TiO_2 capped multilayers. Nb_2O_5 is the best material for capping layer.

Conclusion

- Oxidation durability of Mo/Si multilayer mirrors with oxide capping layer was investigated. Nb_2O_5, TiO_2, RuO_2, MoO_3 were used as oxide capping layer material.
- Reflectance change of Mo/Si multilayer mirrors with oxide capping layer during EUV exposure in water vapor atmosphere was investigated using a synchrotron radiation source.
- Nb_2O_5 capping layer showed the best performance considering oxidation durability and initial reflectance.
- Oxidation of Si layer under the capping layer was observed with XPS even before EUV exposure. The oxidation progresses with EUV irradiation and causes degradation of reflectance. If the oxidation the Si layer can be suppressed, oxidation durability of multilayer mirrors can be further improved.

Acknowledgement

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